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Theoretical Studies of the Extraterrestrial Chemistry

of Biogenic Elements and Compounds

NASA Grant NAG 2-16 • NASA TASK 199-52-12-01

Progress Report

January 1, 1995 - December 31, 1995

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PROGRESS REPORT

1. "A correlated ab initio study of linear carbon-chain radicals C_nH (n=2-7)." D. E. Woon, *Chem. Phys. Lett.* **244**: 45-52 (1995).

   Linear carbon-chain radicals C_nH for n=2-7 were studied with correlation consistent valence and core-valence basis sets and the coupled cluster method RCCSD(T). Equilibrium structures, rotational constants, and dipole moments were determined and compared with available experimental data. The ground state of the even-n series changes from $^2\Sigma^+$ to $^2\Pi$ as the chain is extended. For C_4H, the $^2\Sigma^+$ state was found to lie just 72 cm^{-1} below the $^2\Pi$ state in the estimated complete basis set limit for valence correlation. Core-valence effects stabilize the $^2\Sigma^+$ state by at least another 140 cm^{-1}, however, making the assignment more definitive. The C_2H^- and C_3H^- anions have also been characterized.

2. "Ab initio characterization of MgCCH, $MgCCH^+$, and MgC_2 and pathways to their formation in the interstellar medium." D. E. Woon, *Astrophys. J.* **456:** 602-610 (1996)

   An extensive study of Mg-bearing compounds was performed in order to determine molecular properties critical for planning and executing new astronomical searches and laboratory studies. The primary focus of the work was on MgCCH, $MgCCH^+$, and the isomers of MgC_2. Only MgCCH has been identified in laboratory studies. Additional calculations were carried out on MgH, MgNC, MgCN, and their cations in an effort to evaluate pathways to the formation of MgCCH and $MgCCH^+$ in the ISM or in circumstellar envelopes. Correlated ab initio methods and correlation consistent basis sets were employed. Properties including structures, rotational constants, dipole moments, and harmonic frequencies were determined. The transition state between linear MgCC and cyclic MgC_2 was characterized and found to yield a minimal barrier (~0.5 kcal/mol), indicating easy interconversion of the linear isomer to the more stable cyclic form. Direct reactions in the ISM between ground state Mg or Mg^+ and HCCH are precluded by their large endothermicity, but a number of ion-molecule or neutral-neutral reactions exchange reactions between CCH and various Mg-containing species offer plausible pathways to MgCCH and $MgCCH^+$. Weakly bound MgH may react with CCH to form MgCCH, but MgH has not been detected. Both MgNC and MgCN have been observed, but their reactions with CCH are slightly endothermic by 1-3 kcal/mol. Although MgH^+, $MgNC^+$, and $MgCN^+$ have not been detected, their reactions with CCH to form $MgCCH^+$ are all exothermic. With only a small barrier separating linear MgCC and cyclic MgC_2, the

dissociative recombination of $MgCCH^+$ with an electron is expected to yield cyclic MgC_2 and regenerate Mg and CCH. New astronomical searches for MgCCH, $MgCCH^+$, cyclic MgC_2, $MgNC^+$, and $MgCN^+$ will provide further insight into organo-magnesium astrochemistry.

3. "A correlated *ab initio* study of the $\tilde{X}\ ^2A_1$ and $\tilde{A}\ ^2E$ states of $MgCH_3$ " D.E. Woon, *J. Chem. Phys.* (in press), (1996).

The $\tilde{X}\ ^2A_1$ and $\tilde{A}\ ^2E$ states of the $MgCH_3$ radical have been studied with correlation basis sets and the coupled cluster method RCCSD(T) in order to compare with two recent experimental efforts [M.A. Anderson and L.M. Ziurys, *Astrophys J.* **452**: L157 (1995); R. Rubino, J.M. Williamson, and T.A. Miller, *J. Chem. Phys.* **103**: 5964 (1995)]. The best computed values [RCCSD(T)/cc-pCVTZ] for the $\tilde{X}\ ^2A_1$ state are (experimental results in parentheses): A_e = 160.433 GHz, B_e = 10.948 GHz (B_0 = 11.008 GHz), and μ_e = 1.011 D. The Mg-CH_3 bond is weak, 26.3 kcal/mol. Values for the $\tilde{A}\ ^2E$ state are: A_e = 154.648 GHz (A_0 = 149.666 GHz), B_e = 10.87 GHz (B_0 = 10.932 GHz), and μ_e = 1.022 D. The excitation energy (T_e) for the $\tilde{A}\ ^2E$-$\tilde{X}\ ^2A_1$ transition is 19,999 cm^{-1} (T_{00} = 20,030 cm^{-1}). A brief discussion of bonding trends in Mg-containing radials is included.

4. "On the stability of interstellar carbon clusters: the rate of the reaction between C_3 and O." D. E. Woon and E. Herbst (in press).

New experimental results on the rates of selected neutral-neutral reactions involving either gas phase atoms (C) or radicals (OH, CN) show that these reactions are much more rapid than believed previously. It is currently unclear, however, how general these results are. The results of chemical models of dense interstellar clouds are strongly affected by the inclusion of large numbers of rapid neutral-neutral gas-phase reactions, most of which have not yet been studied in the laboratory. Unstudied reactions involving atomic oxygen and carbon clusters are known to curtail the synthesis of complex molecules if they occur rapidly at low temperatures. In this paper, we show via quantum chemical and dynamical studies that the prototype reaction between O and C_3 possesses a small activation energy barrier, and does not occur rapidly at low temperatures even when tunneling is considered.

5. "Potential energy surfaces for the cyclization of CCN and CCP." D. E. Woon (work in progress).

Although the most stable isomers of CCN and CCP are linear $^2\Pi$ radicals, both have cyclic isomers that lie relatively close in energy. At the RCCSD(T)/cc-pVTZ level, the cyclic isomers lie above the linear forms by only 11.1 and 5.1 kcal/mol for CCN and CCP, respectively. However, the barriers for cyclization are very different, with that of CCN (49.3 kcal/mol) much larger than that of CCP (15.3 kcal/mol). In light of this

difference, it is of interest to examine the relative cyclization rates for vibrationally hot CCN and CCP settling into their cyclic minima rather than the linear ones upon cooling. This process might be encountered, for example, in the dissociative recombination of $HCCN^+$ or $HCCP^+$ with an electron, i.e.,

$$HCCN^+ + e \rightarrow H + CCN^* \; ; \qquad CCN^* \rightarrow CCN \text{ (linear)} + h\nu$$
$$\rightarrow C_2N \text{ (cyclic)} + h\nu$$

The purpose of this ongoing study is to investigate the likelihood of one or both cyclic isomers being present in the interstellar medium.

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Publications

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3. "A correlated *ab initio* study of the $\tilde{X}\ ^2A_1$ and $\tilde{A}\ ^2E$ states of $MgCH_3$ " D.E. Woon, *J. Chem. Phys.* (in press).

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